

PATENT SPECIFICATION

NO DRAWINGS

1,143,481

1,143,481



Date of Application and filing Complete Specification: 21 Feb., 1966.

No. 7597/66.

Application made in United States of America (No. 437,537) on 5 March, 1965.

Complete Specification Published: 19 Feb., 1969.

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Index at acceptance:—C2 C(1Q1A, 1Q2, 1Q3, 1Q4, 1Q5, 1Q6A1, 1Q6B1, 1Q6B2, 1Q6C, 1Q7B, 1Q8A, 1Q8B, 1Q8C, 1Q8D, 1Q9B, 1Q9C, 1Q9F1, 1Q9F2, 1Q9G, 1Q9J, 1Q9K, 1Q9L, 1Q11D, 1Q11G, 1Q11J, P1L2, P3B11A, P3B12B, P3B13, P3B14A, P3B18B, P3B18C, P3B18D, P3B21)

Int. Cl.:—C 07 c 143/08

COMPLETE SPECIFICATION

Fluorocarbon Perfluoroalkanesulfonates

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SPECIFICATION No. 1,143,481

Page 1, Heading, Application made in United States of America, for "(No. 437537)" read "(No. 437573)"

THE PATENT OFFICE
5th May 1969

wherein

R is a hydrogen atom, or a group as herein defined, of 1 to 8 carbon atoms,

Q is a highly fluorinated alkyl group free from hydrogen on valence carbon atoms, having a valence of m and containing at least 44 percent by weight of fluorine, the highly fluorinated alkyl group being a group selected from:

- (a) perfluoroalkyl of 1 to 17 carbon atoms,
- (b) perfluorocycloalkyl of 4 to 11 carbon atoms,
- (c) omega-hydroperfluoroalkyl of an even number of carbon atoms from 2 to 18,
- (d) 2-hydroperfluoroalkyl of 3 to 11 carbon atoms,
- (e) chloro-difluoromethyl,
- (f) 2,2-dichloro-perfluoroethyl,
- (g) 3-oxa-perfluoroalkyl of 3 to 6 carbon atoms and 1 oxygen atom,
- (h) perfluoro-oxa-cycloalkyl of 4 to 6 carbon atoms,
- (i) perfluoroalkylene of 1 to 10 carbon atoms, or
- (j) perfluorocycloalkylene of 6 to 12 carbon atoms, and

m is 1 or 2,

which process comprises reacting substantially stoichiometric amounts of hyperfluorinated alkanesulfonyl halide having the formula:



wherein

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Int. Cl.:—C 07 c 143/08

COMPLETE SPECIFICATION

Fluorocarbon Perfluoroalkanesulfonates

We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 2501 Hudson Road, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to certain sulfonate esters, to a process for producing the sulfonate esters, and to a process using the sulfonate esters in alkylation reactions.

In an article by Burdon and McLoughlin, Tetrahedron, 1965 vol. 21 pp. 1—4 entitled "Trifluoromethanesulfonate Esters and their Alkylating Properties" it is suggested that 2,2,2-trifluoroethyl trifluoromethanesulfonate can be prepared from the alcohol and acid anhydride and is also formed from the alcohol and acid fluoride in the presence of pyridine. Pyridine, however, quaternized with this ester very easily and hence the yield was very poor.

The present invention provides a process for the production of sulfonate esters of the formula:



wherein

R_f is a hyperfluorinated alkyl group (as herein defined) of 1 to 8 carbon atoms, Q is a highly fluorinated alkyl group free from hydrogen on valence carbon atoms, having a valence of m and containing at least 44 percent by weight of fluorine, the highly fluorinated alkyl group being a group selected from:

- (a) perfluoroalkyl of 1 to 17 carbon atoms,
 - (b) perfluorocycloalkyl of 4 to 11 carbon atoms,
 - (c) omega-hydroperfluoroalkyl of an even number of carbon atoms from 2 to 18,
 - (d) 2-hydroperfluoroalkyl of 3 to 11 carbon atoms,
 - (e) chloro-difluoromethyl,
 - (f) 2,2-dichloro-perfluoroethyl,
 - (g) 3-oxa-perfluoroalkyl of 3 to 6 carbon atoms and 1 oxygen atom,
 - (h) perfluoro-oxa-cycloalkyl of 4 to 6 carbon atoms,
 - (i) perfluoroalkylene of 1 to 10 carbon atoms, or
 - (j) perfluorocycloalkylene of 6 to 12 carbon atoms, and
- m is 1 or 2,

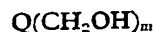
which process comprises reacting substantially stoichiometric amounts of hyperfluorinated alkanesulfonyl halide having the formula:



wherein

SEE ERRATA SLIP ATTACHED

R_1 has the same significance as above, and
 X is Cl or F,
 and highly fluorinated carbinol having the formula:



5 wherein

Q and m have the same significance as above, in the presence of an aliphatic tertiary amine acid acceptor.

Carbinols of the above highly fluorinated alkyl groups are quite well known.

10 In the presence of large excesses of tertiary amine over stoichiometric, quaternization may occur at progressively higher temperatures above room temperature of 25°C. as the molecular weight of the ester increases. Lower temperatures are therefore preferably used particularly in producing esters of trifluoromethanesulfonic acid.

15 As used herein, the term "hyperfluorinated alkyl group" is employed to designate acyclic and cyclic alkyl groups containing at least 2 fluorine atoms and not more than 1 hydrogen atom and containing from 1 to 8 carbon atoms. In particular it is preferred to employ hyperfluorinated alkanesulfonyl fluorides and chlorides in which R_1 is a perfluoroalkyl group of 1 to 8 carbon atoms, perfluorocycloalkyl of 4 to 8 carbon atoms or 2-hydroperfluoroalkyl of 2 to 7 carbon atoms.

This invention also provides sulfonate esters of the formula:



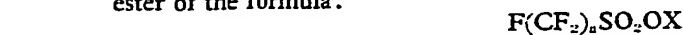
wherein

R_1 is a hyperfluorinated alkyl group (as herein defined) of 1 to 8 carbon atoms,

25 Q' is a highly fluorinated alkyl group free from hydrogen on valence carbon atoms, having a valence of m and containing at least 44 percent by weight of fluorine, the highly fluorinated alkyl group being a group selected from:

- (a) perfluoroalkyl of 2 to 17 carbon atoms,
 - (b) perfluorocycloalkyl of 4 to 11 carbon atoms,
 - (c) omega-hydroperfluoroalkyl of an even number of carbon atoms from 2 to 18,
 - (d) 2-hydroperfluoroalkyl of 3 to 11 carbon atoms,
 - 30 (e) chloro-difluoromethyl,
 - (f) 2,2-dichloro-perfluoroethyl,
 - (g) 3-oxa-perfluoroalkyl of 3 to 6 carbon atoms and 1 oxygen atom,
 - (h) perfluoro-oxa-cycloalkyl of 4 to 6 carbon atoms,
 - (i) perfluoroalkylene of 1 to 10 carbon atoms, or
 - 35 (j) perfluorocycloalkylene of 6 to 12 carbon atoms, and
- m is 1 or 2.

The invention also provides 1,1-dihydroperfluoroalkyl perfluoroalkanesulfonate ester of the formula:

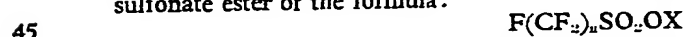


wherein

X is a 1,1-dihydroperfluoroalkyl group of 3 to 18 carbon atoms, and

n is an integer from 1 to 8.

The invention further provides 1,1, ω -trihydroperfluoroalkanol perfluoroalkanesulfonate ester of the formula:

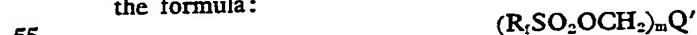


wherein

X is a 1,1, ω -trihydroperfluoroalkyl group of an odd number of carbon atoms from 3 to 19, and

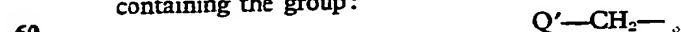
n is an integer from 1 to 8.

50 The invention still further provides a process for introducing a non-fluorinated substituent group on a highly fluorinated organic nucleus, which process comprises combining in mutually compatible medium in substantially stoichiometric proportions a nucleophile having a nucleophilicity constant greater than 1 and sulfonate ester of the formula:



wherein

R_1 , Q' and m have the same significance as above, if desired acid hydrolysing intermediate addition products, and isolating a product containing the group:



wherein

Q' has the same significance as above.

The nucleophile may be the anion of an aryloxy compound, an organic amine, the anion of an organic mercaptan, or the anion of a diorganic ester of orthophosphorous acid.

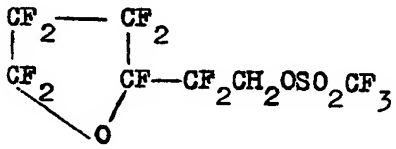
The perfluoroalkane sulfonyl fluorides are readily available by the electrochemical fluorination of the alkane sulfonyl fluorides or chlorides as described in Patent No: 758,467. It is generally preferred to use perfluoromethanesulfonyl fluoride because the cost per mole is lower, but higher sulfonyl fluorides are otherwise satisfactory. Chlorides of 2-hydroperfluorinated acids are described by Coffman and Raasch, Journal of Organic Chemistry, volume 14, page 747 et seq. (1949).

In the following examples, parts are by weight and temperatures are in degrees centigrade unless otherwise indicated.

EXAMPLE 1

In a dried vessel fitted for mechanical agitation a total of 245 parts of trifluoromethanesulfonyl fluoride (B.P. -26°C .) is condensed at about -75°C . To the vessel are added 121 parts by volume of methylene chloride and the equipment is then modified by replacing the gas inlet assembly by a dropping funnel. A mixture of 271 parts of 1,1-dihydroperfluorobutanol and 150 parts of triethylamine is then added gradually over about 1 hour while maintaining the temperature of the reaction mixture at about -40° to -30°C . The reaction mixture is warmed to 0° and the clear solution is washed successively (in parts by volume) with 100 parts of 5 percent aqueous hydrochloric acid, 100 parts of 5 percent aqueous sodium hydroxide and twice with 50 parts of water. The solution is dried over anhydrous magnesium sulfate, filtered and concentrated and finally fractionally distilled to give 1,1-dihydroperfluorobutyl trifluoromethanesulfonate in good yield as a clear colorless liquid boiling at 118° to 120°C . at 732 mm. Hg. pressure, $n_D^{25} = 1.3020$. Analysis: Calculated for $\text{C}_4\text{H}_2\text{F}_{10}\text{O}_3\text{S}$: 12.8% C; Found: 18.3% C.

Other esters of the invention prepared in good yields by the above procedure include the following:

Compound	Boiling Point $^{\circ}\text{C}/\text{mm. Hg. press.}$	n_D^{25}
$\text{CF}_3\text{SO}_2\text{OCH}_2\text{CF}_2\text{CF}_3$	102—5/740	1.3012
$\text{CF}_3\text{SO}_2\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$	74—5/5	1.3098
$\text{CF}_3\text{SO}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$	122—5/737	1.3203
$\text{CF}_3\text{SO}_2\text{OCH}_2(\text{CF}_2)_4\text{H}$	69—72/21	1.3191
$\text{CF}_3\text{SO}_2\text{OCH}_2(\text{CF}_2)_8\text{H}$	117—9/20	1.3200
$\text{CF}_3\text{SO}_2\text{OCH}_2\text{C}_8\text{F}_{11}$	73—6/20	1.3253
$(\text{CF}_3\text{SO}_2\text{OCH}_2\text{CF}_2)_2\text{CF}_2$	76—8/20	1.4252
$\text{CF}_3\text{SO}_2\text{OCH}_2(\text{CF}_2)_2\text{OCF}_3$	120—3/740	1.3070
	64—6/22	1.3167

EXAMPLE 2

The procedure of Example 1 is repeated, except that the sulfonyl fluoride is measured and added as a liquid without the necessity of condensation, using 13.5 parts of perfluoroethanesulfonyl fluoride in 30 parts by volume of methylene chloride at -80° and adding a mixture of 8 parts each of 2,2,2-trifluoroethanol and triethylamine in 20 parts by volume of methylene chloride during about 10 minutes. The

subsequent procedure is as described in Example 1. 2,2,2-Trifluoroethyl perfluoroethanesulfonate is obtained in good yield as a colorless liquid boiling at 105°—6°C. at 740 mm. Hg. pressure, $n_D^{25} = 1.3028$. Analysis: Calculated for $C_4H_2F_8O_3S$: 17.0% C; 53.9% F; Found: 16.8% C; 54.6% F.

By a similar procedure 1,1-dihydroperfluorooctyl perfluorobutanesulfonate is obtained in good yield from the corresponding alcohol and sulfonyl fluoride.

EXAMPLE 3

To a mixture of 25.1 parts of perfluorooctanesulfonyl fluoride in 25 parts by volume of triethylamine in a suitable vessel protected from access of moisture are added 10 parts of 1,1-dihydroperfluorobutanol. The reaction mixture is stirred under reflux for four hours and poured into a mixture of about 25 parts of concentrated hydrochloric acid and 100 parts of ice. The product is extracted with diethylether and the ethereal solution is washed with water and dried. Evaporation of the ether provides an excellent yield of crude 1,1-dihydroperfluorobutyl perfluorooctanesulfonate which is distilled: B.P. 225—7° at 740 mm. Hg. pressure. This ester solidifies slowly and is recrystallized from petroleum ether (b.p. 30° to 60°C.) and then melts at about 59° to 62°C. Analysis: Calculated for $C_{12}H_2F_{22}O_3S$: 21.1% C; 66.9% F; Found: 20.9% C; 66.3% F.

EXAMPLE 4

In a suitable vessel provided with mechanical agitation, thermometer, gas inlet and reflux condenser (cooled to about -75°C.) are placed 332 parts of 1,1,7-trihydroperfluoroheptanol, 120 parts of triethylamine and 500 parts by volume of methylene chloride. The mixture is maintained at about 10° to 20°C. and trifluoromethanesulfonyl fluoride is passed in rapidly over 1 hour until it no longer reacts as evidenced by persistent refluxing thereof when flow of acid fluoride is temporarily discontinued. No further reaction time is needed and the reaction mixture is processed as in Example 1 above.

1,1,7-Trihydroperfluoroheptyl trifluoromethanesulfonate is obtained in good yield as a mobile colorless liquid boiling at 75—8°C. at 9 mm. Hg. pressure, $n_D^{25} = 1.3194$. Analysis: Calculated for $C_8H_3F_{15}O_3S$: 20.6% C; 61.5% F; Found: 20.4% C; 61.2% F.

By the same general procedure employing corresponding proportions of 1,1,11-trihydroperfluoroundecanol, 1,1,11-trihydroperfluoroundecyl trifluoromethanesulfonate is obtained in good yield boiling at 125° to 130°C. at 10 mm. Hg. pressure. It solidifies and is recrystallized from petroleum ether and then melts at about 56° to 59°C.

The examples above describe methods generally adapted to preparing other esters of the invention employing perfluoroalkane sulfonyl fluorides and chlorides of 1 to 8 carbon atoms, perfluorocycloalkane sulfonyl fluorides and chlorides of 4 to 8 carbon atoms (available as described in Patent No: 758,467) and 2-hydroperfluoroalkane sulfonyl chlorides prepared from the acids or salts as described by Coffman and Raasch, supra. Thus, when the appropriate sulfonyl halides, preferably fluorides, are reacted with the carbinols indicated, the esters shown below are obtained.

Carbinol	Product Ester
$ClCF_2-CH_2OH$	$ClCF_2-CH_2-O-O_2SCF_3$
$Cl_2CF-CF_2-CH_2OH$	$Cl_2CF-CF_2-CH_2-O-O_2SCF_3$
$C_5F_{11}-CFH-CF_2-CH_2OH$	$C_5F_{11}-CFH-CF_2-CH_2-O-O_2SCF_3$
CF_3CH_2OH	$CF_3CH_2-O-O_2SCF_2-CF_2H$

As indicated above, the novel esters obtained by the above process are useful as alkylating agents. Thus they may be used for forming substituted fluorocarbons of the formula $Q'(CH_2W)_m$ wherein Q' and m are as herein defined, and W is the nucleus or central portion of a nucleophile, for example the anion of an aryloxy compound or organic mercaptans, or a diorganic ester of orthophosphorous acid or any organic amine and n is 1 or 2.

Examples of nucleophiles having a nucleophilicity constant greater than 1 are:

- (a) monovalent inorganic anions, SCN⁻, Cl⁻, Br⁻ and I⁻;
- (b) anions of aliphatic alcohols of 1 to 20 carbon atoms;
- (c) aliphatic primary, secondary and tertiary amines of 1 to 20 carbon atoms;
- (d) anions of aliphatic mercaptans of 1 to 20 carbon atoms;
- (e) anions of aromatic thiols of 6 to 20 carbon atoms;
- (f) aliphatic primary, secondary or tertiary amines of 1 to 20 carbon atoms;
- (g) aromatic and mixed aralkyl amines of 6 to 20 carbon atoms;
- (h) heterocyclic amines of 2 to 20 carbon atoms;
- (i) anions of aliphatic and alicyclic sulfides of 2 to 12 carbon atoms;
- (j) thiourea;
- (k) anions of active hydrogen compounds of 2 to 20 carbon atoms; including: acetylene, cyclohexyl acetylene, phenyl acetylene, octadecyl acetylene, diethyl malonate, diethyl ethylmalonate, 3-methyl acetylacetone, aceto-acetic ester, cyclopentadiene, phenyl cyclopentyl sulfone, thiolacetic acid, thiolbenzoic acid;
- (l) anions of orthophosphorous acid bis-esters of alcohols and phenols of 1 to 8 carbon atoms, including: dimethyl phosphite, diethyl phosphite, dibutyl phosphite, dioctyl phosphite, diphenyl phosphite, dicesyl phosphite.
- (m) anions of enamines of ketones or aldehydes such as propionaldehyde, cyclopentanone, 1,2,3,4-tetrahydro-2- ketonaphthalene, 5,5- dimethylcyclohexandione- 1,3, cyclodecanone and camphor with secondary amines such as dimethyl amine, morpholine, tetrahydropyridine and piperidine.
- (n) hydrazines containing from 0 to 6 carbon atoms, such as hydrazine, 1,1-dimethylhydrazine, 1,1,2- trimethyl hydrazine, phenyl hydrazine, N- amino piperidine, N, N'- diamino piperazine.
- (o) arene sulfonic acid alkali metal salts.

The concept of a nucleophilic constant was developed by C. G. Swain and C. B. Scott in the Journal of the American Chemical Society, Vol. 75, page 141 *et seq.*, (1953).


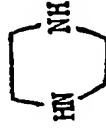
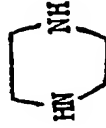

The following examples illustrate this aspect of the invention, with the exception of those examples wherein 2,2,2-trifluoroethyl trifluoromethanesulfonate is employed as the fluoroalkylating agent.

EXAMPLE 5

A mixture of 3.0 parts (0.05 mole) ethylenediamine, 30 parts by volume of dry benzene and 33.2 parts of 1,1-dihydroperfluorobutyl trifluoromethanesulfonate is brought to reflux and 10.1 parts (0.10 mole) of triethylamine are added gradually over 20 minutes. After refluxing for 1 hour further, the solution has become homogeneous and is then cooled, washed twice with water and the benzene phase is dried. Concentration and distillation of the residue provides N,N'-bis-1,1-dihydroperfluorobutyl-ethylenediamine boiling at 97° to 100° at 15 mm. of Hg. pressure, $n_D^{25} = 1.3282$. Analysis: Calculated for C₁₆H₁₀F₁₄N₂: 28.4% C; 62.8% F. Found: 28.1% C; 63.2% F.

Table I shows other amines and their properties prepared by essentially the above procedure employing the reactants indicated:

TABLE I

Compound	Amine	Ester	b.p./mm.	n_D^{25}	m.p.
$CF_3CH_2N(Et)_2$	Et_2NH	$CF_3CH_2OSO_2CF_3$	89—91/740	1.3508	—
$[C_8F_7CH_2NH(CH_2)_3]_2$	$H_2N(CH_2)_6NH_2$	$C_8F_7CH_2OSO_2CF_3$	70—72/20	1.3619	—
$H(CF_2)_6CH_2NHC_4H_9(n)$	$C_4H_9NH_2$	$H(CF_2)_6CH_2OSO_2CF_3$	85—93/8	—	—
$C_7F_{13}CH_2N(CH_2)_2NH$		$C_7F_{13}CH_2OSO_2CF_3$	—	—	72—74
$H(CF_2)_6-CH_2$ 		$H(CF_2)_6CH_2OSO_2CF_3$	—	—	60—62
$H(CF_2)_6-CH_2$ 	$C_3H_7NH_2$	$H(CF_2)_6CH_2OSO_2CF_3$	75—80/10	1.3378	—
$H(CF_2)_6CH_2NHC_3H_7$	$(n-C_4H_9)_2NH$	$H(CF_2)_6CH_2OSO_2CF_3$	105—108/0.3	1.3533	~25
$[H(CF_2)_6CH_2NHCH_2-]_2$	$H_2NCH_2CH_2NH_2$	$H(CF_2)_6CH_2OSO_2CF_3$	—	—	57—58
$[H(CF_2)_6CH_2NH(CH_2)_3]_2$	$H_2N(CH_2)_6NH_2$	$H(CF_2)_6CH_2OSO_2CF_3$	145—150/20	1.3579	—

EXAMPLE 6

5 A suitable vessel is charged with 46.4 parts (0.20 mole) of 1,1-dihydroperfluoroethyl trifluoromethanesulfonate and 32.2 parts (0.44 mole) of diethylamine in 100 parts by volume of benzene. After stirring and refluxing for 1 hour a brownish oil separates which solidifies on cooling at 0°C. It is collected and washed with cold benzene. It is 1,1-dihydroperfluoroethyl diethylammonium trifluoromethanesulfonate. 5

10 The benzene solution and wash are combined and extracted with 100 parts by volume of 10 per cent aqueous hydrochloric acid. The acid extract is washed with ether and neutralized with sodium hydroxide. The oily product is extracted in ether and these extracts are dried over magnesium sulfate, concentrated carefully and distilled through a column. 1,1 - Dihydroperfluoroethyldiethylamine is obtained in 84 percent yield as a liquid boiling at 89° to 91°C. at 740 mm. of Hg. pressure. $n_D^{25} = 1.3508$. The hydrochloride, m.p. 164—5°C., is analyzed. Analysis: Calculated for $C_6H_{13}NF_3Cl$: 37.6% C; 29.7% F; Found: 37.6% C; 29.8% F. 10

EXAMPLE 7

15 A solution in 50 parts by volume of ethanol containing 8 parts of 1,1-dihydroperfluoroethyl trifluoromethanesulfonate, 7 parts of thiophenol and 2 parts of sodium hydroxide in 20 parts of water is refluxed for 1 hour, poured into water and the oily product extracted with ether. After washing and drying, ether is evaporated to give 1,1-dihydroperfluoroethyl phenyl sulfide as a yellowish oil boiling at 83° to 84° at 15 mm. of Hg. pressure, $n_D^{25} = 1.4881$. Analysis: Calculated for $C_8H_7F_3S$: 50.0% C; 29.6% F; Found: 49.7% C; 29.5% F. 15

20 By a similar procedure 1,1-dihydroperfluoroethyl trifluoromethanesulfonate is reacted with phenol (C_6H_5OH) to give 2',2',2'-trifluoroanethole ($C_6H_5OCH_2CF_3$) as a liquid with $n_D^{25} = 1.4376$ and boiling at 55° to 58°C. at 10 mm. Hg. pressure. 20

25 By following essentially the above procedures 1,1-dihydroperfluoroalkyl ethers of the phenols are prepared using the reactants given in Table II. 25

Table II

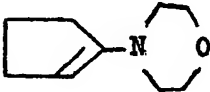
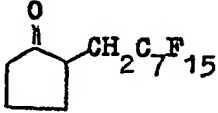
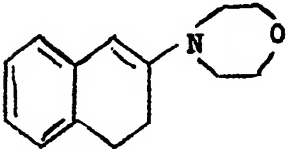
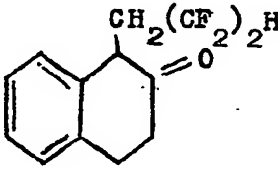
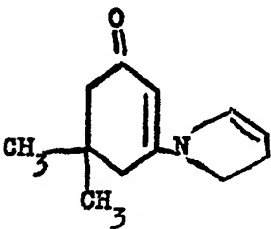
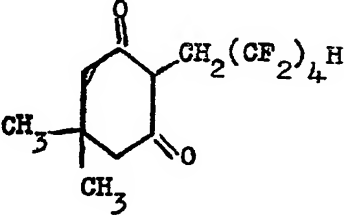
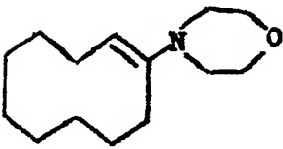
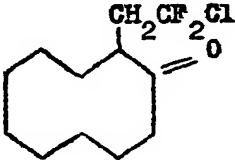
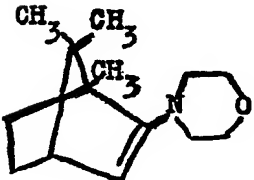
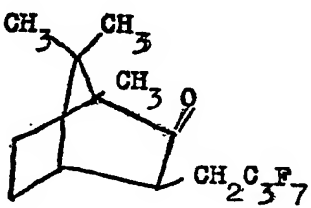
<u>Ester</u>	<u>Phenol</u>	<u>Product</u>
$C_7F_{15}CH_2OSO_2CF_3$		$C_7F_{15}CH_2O$
5 $C_7F_{15}CH_2OSO_2CF_3$		$C_7F_{15}CH_2O$
$C_3F_7CH_2OSO_2CF_3$		
$H(CF_2)_8CH_2OSO_2CF_3$		O_2N
10 $H(CF_2)_2CH_2OSO_2CF_3$		
$C_7F_{15}CH_2OSO_2CF_3$		
15 $C_7F_{15}CH_2OSO_2CF_3$		$\left[C_7F_{15}CH_2O \right]_2 C(CH_3)_2$
$H(CF_2)_6CH_2OSO_2CF_3$		$H(CF_2)_6CH_2O$

EXAMPLE 8

5 A solution of 3.3 parts of cyclohexanone piperidine-eneamine in 50 parts by volume of 1,2-dimethoxyethane is added to 4.68 parts of 1,1,7-trihydroperfluoroheptyl trifluoromethanesulfonate in a suitable vessel and the mixture is refluxed for 4 hours with agitation. To the cooled mixture are added 10 parts by volume of concentrated hydrochloric acid and the mixture is poured on ice and extracted with ether. The ethereal solution is washed with water, 10 percent aqueous sodium bicarbonate, dried and concentrated. Distillation of the residue yields 2-(1',1',7'-trihydroperfluoroheptyl)-cyclohexanone boiling at 100° to 110°C. at 20 mm. of Hg. pressure. It forms a 2,4-dinitrophenylhydrazone melting at 143° to 145°C.

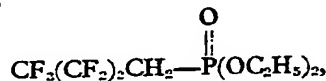
10 Other eneamines, as shown in Table III, are employed in corresponding proportions with perfluoroalkanesulfonate esters to provide the indicated novel fluorinated carbonyl compounds.

TABLE III

Enamine	Ester	Product
$\text{CH}_3\text{CH}=\text{CH}-\text{N}(\text{CH}_3)_2$	$\text{CF}_3\text{CH}_2\text{OSO}_2\text{CF}_3$	$\text{CF}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CHO}$
	$\text{C}_7\text{F}_{15}\text{CH}_2\text{OSO}_2\text{CF}_3$	
	$\text{H}(\text{CF}_2)_2\text{CH}_2\text{OSO}_2\text{CF}_3$	
	$\text{H}(\text{CF}_2)_4\text{CH}_2\text{OSO}_2\text{CF}_3$	
	$\text{CF}_2\text{ClCH}_2\text{OSO}_2\text{CF}_3$	
 (Camphor enamine)	$\text{C}_3\text{F}_7\text{CH}_2\text{OSO}_2\text{CF}_3$	

EXAMPLE 9

Diethyl hydrogen phosphite ($\text{HOP}(\text{OC}_2\text{H}_5)_2$; 47 parts) in 200 parts by volume of tetrahydrofuran is reacted during one hour with 7.5 parts of sodium metal. The solution is maintained at 25° and during a second hour 107 parts of 1,1-dihydroperfluorobutyl trifluoromethanesulfonate are added gradually: the solution is then refluxed for another hour. Reaction occurs by alkylation of the phosphorus atom. The reaction mixture is quenched in water and extracted with benzene. The extract is washed with water, dried, concentrated and the residue distilled. Diethyl 1,1-dihydroperfluorobutanephosphonate,



boils at about 72° to 72.5°C . at 2.5 mm. of Hg. pressure, $n_D^{25} = 1.3489$. Analysis: Calculated for $\text{C}_8\text{H}_{12}\text{F}_4\text{O}_3\text{P}$: 30.0% C; 3.7% H; Found: 29.7% C; 3.4% H.

By a similar procedure employing 1,1-dihydroperfluorooctyl trifluoromethanesulfonate, diethyl 1,1-dihydroperfluorooctanephosphonate, is obtained as a liquid having $n_D^{25} = 1.3486$ boiling at about 91° to 96°C . at 0.35 mm. of Hg. pressure. Other sulfonate esters and phosphite esters react to produce esters of other fluorinated alkanephosphonates as indicated in Table IV.

TABLE IV

Sulfonate ester	Phosphite ester	Product: dialkyl fluorinated phosphonate
$\text{C}_7\text{F}_{15}\text{CH}_2\text{OSO}_2\text{CF}_3$	$\text{HOP}(\text{OC}_4\text{H}_9)_2$	$\text{C}_7\text{F}_{15}\text{CH}_2\text{P}(\text{O})(\text{OC}_4\text{H}_9)_2$
$\text{C}_7\text{F}_{15}\text{CH}_2\text{OSO}_2\text{C}_2\text{F}_5$	$\text{HOP}(\text{OC}_6\text{H}_5)_2$	$\text{C}_7\text{F}_{15}\text{CH}_2\text{P}(\text{O})(\text{OC}_6\text{H}_5)_2$
$\text{H}(\text{CF}_2)_{10}\text{CH}_2\text{OSO}_2\text{CF}_3$	$\text{HOP}(\text{OCH}_3)_2$	$\text{H}(\text{CF}_2)_{10}\text{CH}_2\text{P}(\text{O})(\text{OCH}_3)_2$
$\text{CF}_2(\text{CF}_2\text{CH}_2\text{OSO}_2\text{CF}_3)_2$	$\text{HOP}(\text{OC}_2\text{H}_5)_2$	$\text{CF}_2[\text{CF}_2\text{CH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$
A compound of the formula $\text{cycl}-(\text{C}_5\text{F}_9\text{O})-\text{CH}_2\text{OSO}_2\text{CF}_3$	$\text{HOP}(\text{OC}_8\text{H}_{17})_2$	$\text{cycl}-(\text{C}_5\text{F}_9\text{O})-\text{CH}_2\text{P}(\text{O})(\text{OC}_8\text{H}_{17})_2$

The product dialkyl fluorinated phosphonates are readily hydrolyzed to the corresponding strong acids, converted to salts with, e.g. alkali metals, and to amides. They find utility as corrosion inhibitors, surfactants and as additives to oils.

The following examples further illustrate the use of esters of the invention particularly for the production of halides, tertiary amines and lower alkyl ethers. These examples further show the unexpected superiority of the esters of the invention with regard to reaction rates as compared to the known alkyl and aryl perfluoroalkanesulfonates.

EXAMPLE 10

The rate of methanolysis of 1,1-dihydroperfluoroethyl trifluoromethanesulfonate to give 1,1-dihydroperfluoroethyl methyl ether is followed by usual methods at 100°C . and first order integrated reaction rate constant is calculated from the data to be $4.28 \pm 0.14 \times 10^{-5}$ reciprocal seconds. The half-life of the methanolysis at 100°C . is about 4.4 hours. Reaction constants of about the same order of magnitude are determined for other highly fluorinated alkyl perfluoroalkane sulfonates as shown in Table V.

TABLE V

Ester	K_1 (reciprocal seconds)
$\text{CF}_3\text{SO}_2\text{OCH}_2\text{CF}_2\text{CF}_3$	$1.01 \pm 0.01 \times 10^{-5}$
$\text{CF}_3\text{SO}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_3$	$0.631 \pm 0.006 \times 10^{-5}$
$\text{CF}_3\text{SO}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$	$6.46 \pm 0.04 \times 10^{-5}$
$\text{CF}_3\text{CF}_2\text{SO}_2\text{OCH}_2\text{CF}_3$	$6.76 \pm 0.1 \times 10^{-5}$

By contrast to the above, non-fluorinated alkyl esters, e.g., methyl trifluoromethanesulfonate, are very readily alcoholized, and aryl esters, such as phenyl or *p*-nitrophenyl trifluoromethanesulfonate or anisyl perfluorooctanesulfonate show no appreciable alcoholysis in 24 hours at 96°C.

EXAMPLE 11

The perfluoroalkane sulfonate esters of the invention are very useful for the production of the 1-halides of the polyfluorinated alcohols. The reaction proceeds much more readily than is the case when tosylates are used as described by Tiers, Brown and Reid, Journal of the American Chemical Society, vol. 75, pages 5978—9 (1953). The procedures described here are exemplary of procedures employing other alkali metal halides as well as other sulfonate esters of the invention.

A suitable vessel fitted with thermometer, distillation head and mechanical agitation is charged with 30 parts (0.2 moles) of sodium iodide and 100 parts by volume of anhydrous acetone. The temperature rises to 35° and 23.2 parts (0.1 mole) of 1,1-dihydroperfluoroethyl trifluoromethanesulfonate are then added. The temperature rises further to 50° in 5 minutes and falls to 40° over 1.5 hours. The reaction mixture is poured onto ice and the heavier organic phase separated, washed with a small amount of aqueous sodium thiosulphate to remove iodine, dried and distilled. 1,1-Dihydroperfluoroethyl iodide boils at 60—61° at atmospheric pressure.

In experiments to determine the rate of reaction of 1,1-dihydroperfluoroethyl trifluoromethanesulfonate with iodide ion in acetone at 25°C, it is found that the second order rate constant is about .0149±.003 liters per mole-second. The rate constant for the reaction of 1,1-dihydroperfluoroethyl bromide with iodide ion is extrapolable to comparable conditions from the results of McBee and coworkers, Journal of the American Chemical Society, vol. 84, page 3157 (1962) and is found to be slower by about five orders of magnitude, i.e., 100,000 times.

EXAMPLE 12

The reaction of the perfluoroalkane sulfonate esters with alkali metal salts of *p*-toluenesulfonic and other substituted and unsubstituted arenesulfonic acids readily leads to esters of the aromatic acids.

Two parts of lithium *p*-toluenesulfonate and 2.0 parts of the 1,1-dihydroperfluorobutyl trifluoromethanesulfonate of Example 1 are dissolved in 8 parts by volume of dimethylformamide and the solution is heated to 120°C. A vigorous reaction occurs and the reaction mixture is refluxed for a further 0.5 hour, cooled and poured into cold water. The aqueous suspension is extracted with ether, and the organic phase is washed with salt solution, dried over anhydrous magnesium sulfate and concentrated. The residual oil is distilled at 65° to 75° at 1 mm. Hg. pressure to give 1,1-dihydroperfluorobutyl *p*-toluenesulfonate which eventually solidifies and then melts at 28° to 29°C.

Esters of other fluorinated carbinols with arenesulfonic acids are prepared by the same procedure employing alkali metal salts of the desired substituted or unsubstituted arene-sulfonic acid in the above procedure. This may provide a convenient expedient for the modification of dyestuffs containing sulfonic acid groups to introduce at least slight fluorocarbon solubility.

EXAMPLE 13

This example further illustrates the utility of the invention in reactions with anionic nucleophiles. A mixture of 25 parts of 1,1-dihydroperfluorooctyl trifluoromethanesulfonate of Example 1 and 10 parts of potassium thiocyanate in 80 parts by volume of isopropanol is refluxed for 4 hours. After cooling, the solution and precipitate are poured into an excess of water and the organic precipitate is collected and dried under reduced pressure at 50°C. Recrystallization from a mixture of ether and petroleum ether gives 1,1-dihydroperfluorooctyl thiocyanate melting at about 63° to 66°C. Calculated for $C_8H_2F_{15}NH$: 24.5% C; 64.6% F; Found: 24.4% C; 64.6% F.

This novel fluorinated thiocyanate is representative of the series of compounds obtained when other of the above described perfluoroalkanesulfonate esters of the formula $(R_1SO_2OCH_2)_2Q'$ are used in the above procedure. These thiocyanates are useful intermediates for conversion to 1,1-dihydroperfluoroalkyl sulfur compounds.

EXAMPLE 14

This example illustrates the preparation of dihydroperfluoroalkyl hydrazines. A mixture of 26.6 parts of 1,1-dihydroperfluorooctyl trifluoromethanesulfonate from Example 1, 5 parts of 95 percent hydrazine and 75 parts by volume of isopropanol is refluxed with stirring for 3 hours and the reaction mixture poured into water. The solution is extracted with ether. The ethereal extract is washed with saline solution and dried. Saturation of the ethereal solution with anhydrous hydrogen chloride precipitates 1,1-dihydroperfluorooctyl hydrazine hydrochloride melting at about 231° to 233°C. The free base, 1,1-dihydroperfluorooctyl hydrazine is liberated by 10 percent aqueous sodium hydroxide as an oil which is distilled at 73°—75°C. at 5 mm. Hg. pressure. Calculated for $C_8F_{15}H_5N_2$: 23.3% C; 69.0% F; Found: 23.2% C; 68.1% F. When the above procedure is repeated employing other highly fluorinated perfluoroalkane sulfonates, other hydrazines of the series $Q'(CH_2NHNH_2)_m$ are obtained. Substituted hydrazines, for example phenylhydrazine, are also suitable in the above procedure giving hydrazines of the series $Q'(CH_2NHNHR)_m$ wherein R is unsubstituted or substituted alkyl, aryl or aralkyl as shown in Table VI.

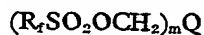
TABLE VI

Sulfonate ester	Product hydrazine
$C_7F_{15}CH_2OSO_2CF_3$	$C_7F_{15}CH_2NH-N(CH_3)_2$
$C_3F_7CH_2OSO_2CF_3$	$C_3F_7CH_2NH-NH-\begin{array}{c} CH_2-CH_2 \\ \quad \\ CH_2-CH_2 \end{array}-N-NH-CH_2-C_3F_7$
$C_3F_7CH_2OSO_2C_2F_5$	$C_3F_7CH_2-NH-NH-C_6H_5$
$C_7F_{15}CH_2OSO_2CF_3$	$C_7F_{15}CH_2-NH-N-\begin{array}{c} CH_2-CH_2 \\ \quad \\ CH_2-CH_2 \end{array}-CH_2$
$C_3F_7CH_2OSO_2CF_3$	$C_3F_7CH_2-NH-NH-CH_2C_3F_7$
$(CF_2)_2(CH_2OSO_2CF_3)_2$	$(CF_2)_2(CH_2NHNHC_6H_5)_2$
A compound of the formula $cycl-(C_3F_7O)-CH_2OSO_2CF_3$	$cycl-(C_3F_7O)-CH_2-N(CH_3)-N(CH_3)_2$

These hydrazines are useful chemical intermediates.

WHAT WE CLAIM IS:—

1. A process for the production of sulphonate esters of the formula:



wherein

- 5 R_f is a hyperfluorinated alkyl group (as herein defined) of 1 to 8 carbon atoms, 5
 Q is a highly fluorinated alkyl group free from hydrogen on valence carbon atoms, having a valence of m and containing at least 44 percent by weight of fluorine, the highly fluorinated alkyl group being a group selected from:
- 10 (a) perfluoroalkyl of 1 to 17 carbon atoms, 10
 (b) perfluorocycloalkyl of 4 to 11 carbon atoms,
 (c) omega-hydroperfluoroalkyl of an even number of carbon atoms from 2 to 18,
 (d) 2-hydroperfluoroalkyl of 3 to 11 carbon atoms,
 (e) chloro-difluoromethyl,
 (f) 2,2-dichloro-perfluoroethyl,
 15 (g) 3-oxa-perfluoroalkyl of 3 to 6 carbon atoms and 1 oxygen atom, 15
 (h) perfluoro-oxa-cycloalkyl of 4 to 6 carbon atoms,
 (i) perfluoroalkylene of 1 to 10 carbon atoms, or
 (j) perfluorocycloalkylene of 6 to 12 carbon atoms, and
 m is 1 or 2,
- 20 which process comprises reacting substantially stoichiometric amounts of hyper- 20
 fluorinated alkanesulfonyl halide having the formula:



wherein

- 25 R_f has the same significance as above, and 25
 X is Cl or F,
 and highly fluorinated carbinol having the formula:



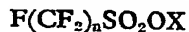
wherein

- 30 Q and m have the same significance as above, in the presence of an aliphatic 30
 tertiary amine acid acceptor.
2. A process according to claim 1 in which the acid acceptor is triethylamine.
3. Sulfonate esters of the formula:



wherein

- 35 R_f is a hyperfluorinated alkyl group (as herein defined) of 1 to 8 carbon atoms, 35
 Q' is a highly fluorinated alkyl group free from hydrogen on valence carbon atoms, having a valence of m and containing at least 44 percent by weight of fluorine, the highly fluorinated alkyl group being a group selected from:
- 40 (a) perfluoroalkyl of 2 to 17 carbon atoms, 40
 (b) perfluorocycloalkyl of 4 to 11 carbon atoms,
 (c) omega-hydroperfluoroalkyl of an even number of carbon atoms from 2 to 18,
 (d) 2-hydroperfluoroalkyl of 3 to 11 carbon atoms,
 (e) chloro-difluoromethyl,
 (f) 2,2-dichloro-perfluoroethyl,
 45 (g) 3-oxa-perfluoroalkyl of 3 to 6 carbon atoms and 1 oxygen atom, 45
 (h) perfluoro-oxa-cycloalkyl of 4 to 6 carbon atoms,
 (i) perfluoroalkylene of 1 to 10 carbon atoms, or
 (j) perfluorocycloalkylene of 6 to 12 carbon atoms, and
 m is 1 or 2.
- 50 4. 1,1-dihydroperfluoroalkyl perfluoroalkanesulfonate ester of the formula: 50



wherein

- 55 X is a 1,1-dihydroperfluoroalkyl group of 3 to 18 carbon atoms, and 55
 n is an integer from 1 to 8.
5. 1,1, ω -trihydroperfluoroalkanol perfluoroalkanesulfonate ester of the formula:



wherein

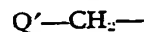
X is a 1,1,*n*-trihydroperfluoroalkyl group of an odd number of carbon atoms from 3 to 19, and

n is an integer from 1 to 8.

5 6. A process for introducing a non-fluorinated substituent group on a highly fluorinated organic nucleus, which process comprises combining in mutually compatible medium in substantially stoichiometric proportions a nucleophile having a nucleophilicity constant greater than 1 and sulfonate ester of the formula:



10 wherein R_f , Q' and *m* have the same significance as in claim 3, if desired acid hydrolysing intermediate addition products, and isolating a product containing the group:



15 wherein Q' has the same significance as in claim 3.

7. A process according to claim 6 wherein the nucleophile is the anion of an aryloxy compound.

8. A process according to claim 6 wherein the nucleophile is an organic amine.

20 9. A process according to claim 6 wherein the nucleophile is the anion of an organic mercaptan.

10. A process according to claim 6 wherein the nucleophile is the anion of a diorganic ester of orthophosphorous acid.

11. A process according to claim 1 substantially as herein described.

12. Sulfonate esters according to claim 3 substantially as herein described.

25 13. A process according to claim 6 substantially as herein described.

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